

Self-avoiding walks adsorbed at a surface and pulled at their mid-point

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Abstract. We consider a self-avoiding walk on the d -dimensional hypercubic lattice, terminally attached to an impenetrable hyperplane at which it can adsorb. When a force is applied the walk can be pulled off the surface and we consider the situation where the force is applied at the middle vertex of the walk. We show that the temperature dependence of the critical force required for desorption differs from the corresponding value when the force is applied at the end-point of the walk. This is of interest in single molecule pulling experiments since it shows that the required force can depend on where the force is applied. We also briefly consider the situation when the force is applied at other interior vertices of the walk.

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1. Introduction

Self-avoiding walks are the standard model of the configurational properties of long linear polymers in dilute solution [11, 21]. The situation can be adapted to model the adsorption of linear polymers at an impenetrable surface [5, 10, 15, 23] and the general features of the adsorption behaviour are now quite well understood. With the invention of micro-manipulation techniques such as atomic force microscopy (AFM) and optical tweezers that allow individual polymer molecules to be pulled [7, 26] there has been renewed interest in how polymers respond to a force and, specifically, how self-avoiding walk models of polymers respond to a force [1, 2, 8, 9, 14, 17]. There has also been some work on how lattice polygons (a model of ring polymers) respond to a force [2, 12, 13].

In this paper we shall be concerned with self-avoiding walks adsorbed at a surface and pulled off the surface (*i.e.* desorbed) by the application of a force. The case that has received most attention is a self-avoiding walk on the d -dimensional hypercubic lattice \mathbb{Z}^d , attached at one end point to an impenetrable surface at which it can adsorb. A force, normal to the surface, is applied at the other vertex of degree 1 (*i.e.* at the other end point of the walk) and this force is increased until the walk desorbs from the surface [3, 16, 19, 20, 22]. At a particular temperature T (below the critical temperature for adsorption) there is a critical value of the force, $f_c(T)$. If the applied force is less than $f_c(T)$ the walk is adsorbed while if the force is greater than $f_c(T)$ the walk is desorbed into a ballistic phase. If $d \geq 3$ then the force-temperature curve is reentrant, *i.e.* the critical force initially increases as the temperature is increased at low temperature [16, 19, 20, 22]. The walk has entropy in the adsorbed state and this entropy is lost at low temperature when the walk is pulled off the surface. The reentrance is associated with the force required to compensate for this entropy loss. See also [24] and [25] for related work. In two dimensions the critical force is a monotone decreasing function of the temperature [3, 19, 20, 22]. For all $d \geq 2$ the phase transition from the adsorbed to the ballistic phase is first order [3].

In an AFM experiment, unless special precautions are taken, the AFM tip can be in contact with different monomers, not just the last monomer. Consequently it is natural to ask how the behaviour depends on where on the polymer the force is being applied. Apart from the case discussed above where the force is applied at the last monomer the only situation that has been studied [2, 17, 18] is as follows. Suppose that we imagine a plane, parallel to the adsorbing plane, containing the monomers that are furthest away from the adsorbing plane, and apply the force either to pull this plane away from or push it towards the adsorbing surface. We can think of the force as being conjugate to the span of the polymer in the direction normal to the adsorbing plane. Beaton *et al* [2] looked at the situation where there is no interaction with the adsorbing plane (except that it is impenetrable) and considered pushing towards this plane. They used ideas from SLE to make some predictions in two dimensions, and checked these by exact enumeration and series analysis. They discovered interesting sub-exponential behaviour that causes slow convergence to the limiting behaviour. The limiting behaviour when there is a surface interaction and a force has also been investigated [18].

In this paper we are looking at the situation illustrated in figure 1, where the adsorbing polymer is pulled in its midpoint from the adsorbing surface. This is modelled by a self-avoiding walk as shown in figure 2: The force is applied at the midpoint of the walk, and vertices of the walk interact with the adsorbing surface with activity a .

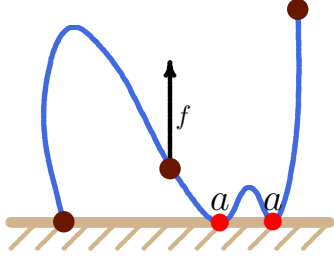


Figure 1. An adsorbing polymer pulled at its midpoint by a force f in the vertical direction. Monomers in the polymer adsorb in the hard wall with activity a .

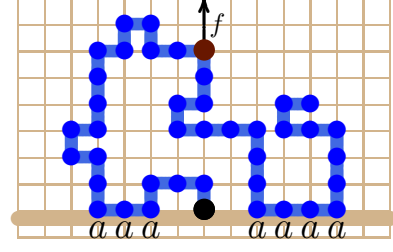


Figure 2. An adsorbing walk pulled at its midpoint by a force f in the vertical direction. Monomers in the walk interact with the hard wall with activity a .

2. Some notation and a brief review

Consider the d -dimensional hypercubic lattice \mathbb{Z}^d and attach the obvious coordinate system (x_1, x_2, \dots, x_d) so that each vertex has integer coordinates. The hyperplane $x_d = 0$ will be the distinguished plane at which adsorption can occur. A *positive walk* is a self-avoiding walk that starts at the origin and has $x_d \geq 0$ for all vertices of the walk, so that it is confined to be in or on one side of $x_d = 0$. Let $c_n^+(v, h)$ be the number of n -edge positive walks with $v + 1$ vertices in $x_d = 0$ and with the x_d -coordinate of the last vertex equal to h . We call h the *height* of the last vertex and we say that the walk has v *visits*. Define the partition function

$$C_n^+(a, y) = \sum_{v, h} c_n^+(v, h) a^v y^h. \quad (1)$$

We can write $a = e^{-\epsilon/k_B T}$ and $y = e^{f/k_B T}$ where ϵ is the energy associated with a vertex in the surface, k_B is Boltzmann's constant, T is the absolute temperature and f is the force applied to the last vertex, measured in energy units. For adsorption to occur ϵ must be negative so $a > 1$. A force directed away from the surface corresponds to $f > 0$ or $y > 1$. It is known [16] that the limit $\lim_{n \rightarrow \infty} \frac{1}{n} \log C_n^+(a, y) \equiv \psi(a, y)$ exists for all a and y . We shall write $\psi(a, 1) = \kappa(a)$ and $\psi(1, y) = \lambda(y)$. $\kappa(a)$ is the free energy of an adsorbing walk in the absence of a force [5] and $\lambda(y)$ is the free energy of a walk subject to a force but not interacting with the surface [1]. $\kappa(a)$ is a convex function of $\log a$ and there is a critical value of a , $a_c > 1$, such that $\kappa(a) = \log \mu_d$ when $a \leq a_c$ and $\kappa(a) > \log \mu_d$ when $a > a_c$ [5]. Here μ_d is the growth constant of self-avoiding walks on \mathbb{Z}^d [4]. Similarly $\lambda(y)$ is a convex function of $\log y$ [14], equal to $\log \mu_d$ when $y \leq 1$ and greater than $\log \mu_d$ when $y > 1$ [1]. See also [8, 9]. We know that [16]

$$\psi(a, y) = \max[\kappa(a), \lambda(y)] \quad (2)$$

so, when $a > a_c$ and $y > 1$, there is a phase boundary in the (a, y) -plane determined by the solution of the equation $\kappa(a) = \lambda(y)$, between an adsorbed phase and a ballistic phase. This phase transition is first order [3].

If the walk is pulled or pushed at its top plane then we need to keep track of the span of the walk in the x_d -direction. Let $c_n(v, s)$ be the number of n -edge positive walks with $v + 1$ vertices in

$x_d = 0$ and with span in the x_d -direction equal to s . Define the partition function

$$C_n(a, y) = \sum_{v, s} c_n(v, s) a^v y^s. \quad (3)$$

The limit $\lim_{n \rightarrow \infty} \frac{1}{n} \log C_n(a, y)$ exists and is equal to $\psi(a, y)$ [18] so, in the infinite n limit, the free energy is identical to the free energy when the force is applied at the last vertex. There are, however, major differences in the finite size behaviour [2, 14].

Are there situations where the location where the force is applied leads to different behaviour? In this paper we shall show that there are. We focus on the effect of applying the force at the middle vertex of the walk, although we shall show in Section 7 that, in some circumstances, our results generalize in a natural way to pulling at other interior vertices, while in other circumstances there is an additional phase in the phase diagram.

Number the vertices of the walk $0, 1, 2, \dots, n$. We define the *middle vertex* to be the vertex numbered $\frac{1}{2}n$ if n is even and $\frac{1}{2}(n-1)$ if n is odd. Let $w_n(v, h)$ be the number of n -edge positive walks with $v+1$ vertices in $x_d = 0$ and with the x_d -coordinate of the middle vertex equal to h . We call h the *height* of the middle vertex. Define the partition function

$$W_n(a, y) = \sum_{v, h} w_n(v, h) a^v y^h. \quad (4)$$

We shall show that the limit

$$\lim_{n \rightarrow \infty} \frac{1}{n} \log W_n(a, y) \equiv \phi(a, y) \quad (5)$$

exists for all a and y , and explore its relation to $\psi(a, y)$. In particular we shall show that the two free energies are not equal in some regions of the (a, y) -plane. In fact, as we shall see, the two free energies are equal in the *free phase* when $0 \leq a \leq a_c$ and $0 \leq y \leq 1$ (see Section 3), and in the adsorbed phase, but not in the ballistic phase (see Section 5). Consequently the phase boundary between the adsorbed and ballistic phases is different when the walk is pulled at the middle and at the end vertex.

A *bridge* is a positive walk with the extra conditions that

- (i) The first edge is in the x_d -direction, and
- (ii) The x_d -coordinate of the last vertex is at least as large as that of any other vertex.

Let $b_n(h)$ be the number of n -edge bridges with the x_d -coordinate of the last vertex being h , and define the partition function as $B_n(y) = \sum_h b_n(h) y^h$. Then $\lim_{n \rightarrow \infty} \frac{1}{n} \log B_n(y) = \lambda(y)$ [17].

Define a *loop* to be a positive walk with both vertices of degree 1 in $x_d = 0$. Let $l_n(v, s)$ be the number of n -edge loops with $v+1$ vertices in $x_d = 0$ and with span in the x_d -direction equal to s . Write $L_n(a, y) = \sum_{v, s} l_n(v, s) a^v y^s$ for the partition function of loops with y conjugate to the span in the x_d -direction. Then [5] $\lim_{n \rightarrow \infty} \frac{1}{n} \log L_n(a, 1) = \kappa(a)$. Since the end vertices of a walk can be somewhat inaccessible we shall often find it useful to work with unfolded walks [6] and we recall some results about unfolded objects of various types. Write $x_i(j)$ for the i th coordinate of the j th vertex of an n -edge walk or loop, $1 \leq i \leq d$, $0 \leq j \leq n$. A loop is *unfolded* if $x_1(0) \leq x_1(j) < x_1(n)$ for all $0 < j < n$ and we write $L_n^\ddagger(a, y)$ for the partition function of unfolded loops (with y conjugate to the span in the x_d -direction). In a similar way we write $W_n^\ddagger(a, y)$ for the partition function of unfolded walks pulled at their mid-point (with y conjugate to the height of the middle vertex) and

$C_n^\dagger(a, y)$ for the partition function of unfolded positive walks (with y conjugate to the height of the last vertex). For these three cases we have [5, 6],

$$\begin{aligned} L_n^\dagger(a, y) &\leq L_n(a, y) \leq e^{O(\sqrt{n})} L_n^\dagger(a, y); \\ C_n^\dagger(a, y) &\leq C_n^+(a, y) \leq e^{O(\sqrt{n})} C_n^\dagger(a, y); \\ W_n^\dagger(a, y) &\leq W_n(a, y) \leq e^{O(\sqrt{n})} W_n^\dagger(a, y). \end{aligned} \quad (6)$$

Hence $\lim_{n \rightarrow \infty} \frac{1}{n} \log L_n^\dagger(a, y) = \lim_{n \rightarrow \infty} \frac{1}{n} \log L_n(a, y)$, and similarly for $C_n(a, y)$ and $W_n(a, y)$. In a similar way we write $B_n^\dagger(y)$ for the partition function of unfolded bridges, and

$$B_n^\dagger(y) \leq B_n(y) \leq e^{O(\sqrt{n})} B_n^\dagger(y). \quad (7)$$

3. Walks pushed towards the surface at their middle vertex

In this section we consider the situation where the middle vertex is being pushed towards the surface. That is, $f < 0$ or $y < 1$. When $y = 1$ [5] we know that

$$\lim_{n \rightarrow \infty} \frac{1}{n} \log L_n^\dagger(a, 1) = \lim_{n \rightarrow \infty} \frac{1}{n} \log C_n^\dagger(a, 1) = \kappa(a). \quad (8)$$

Theorem 1. *For all $a > 0$ and $y \leq 1$ the free energy of walks with the force applied at the middle vertex is equal to the free energy of walks with the force applied at the end vertex. Moreover, this free energy is independent of y . That is, $\phi(a, y) = \psi(a, y) = \psi(a, 1) = \kappa(a)$ for all $a > 0$ when $y \leq 1$.*

Proof: When there is no force it is clear that $\phi(a, 1) = \kappa(a) = \psi(a, 1)$. Fix $y < 1$. By monotonicity $W_n(a, 0) \leq W_n(a, y) \leq W_n(a, 1)$ and therefore

$$\limsup_{n \rightarrow \infty} \frac{1}{n} \log W_n(a, y) \leq \kappa(a) = \psi(a, 1). \quad (9)$$

To get a bound in the other direction note that, for all $a > 0$,

$$W_n(a, y) \geq W_n(a, 0) \geq L_{\lfloor n/2 \rfloor}^\dagger(a, 1) C_{n - \lfloor n/2 \rfloor}^\dagger(a, 1), \quad (10)$$

by the construction in figure 3. Hence

$$\liminf_{n \rightarrow \infty} \frac{1}{n} \log W_n(a, y) \geq \kappa(a) = \psi(a, 1) \quad (11)$$

for all $a > 0$. Then (9) and (11) complete the proof. \square

In particular, when $0 < a \leq a_c$ and $y \leq 1$ the free energy is equal to $\log \mu_d$. This is the *free phase*.

4. Walks repelled from the surface

The case $0 < a \leq 1$ and $0 < y \leq 1$ in Section 3 is of walks with midpoint pushed towards the surface. We now look at the case $0 < a \leq 1$ and $y \geq 1$ (when walks repelled from the surface are also pulled at their midpoint from the surface).

The idea in this section is to relate walks with any number of visits to walks with no visits by translating the walk a unit distance in the x_d -direction, and adding an edge to reconnect it to the origin. Since we are pulling at the mid-point there is a complication in that we want the two subwalks (that meet at the midpoint) to be of equal length so we have to add an additional edge. This can be conveniently accomplished if we work with unfolded walks.

We first look at the case $a = 1$ where there is no interaction with the surface.

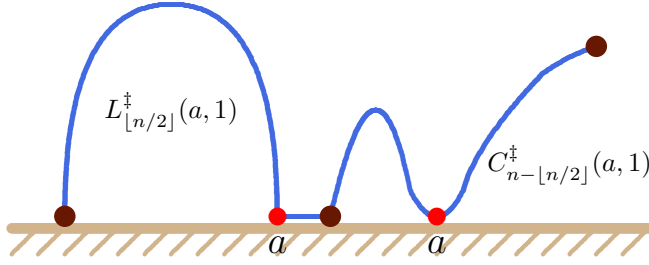


Figure 3. Concatenating an unfolded adsorbing loop with an unfolded walk gives a lower bound on $W_n(a, 0)$ (that is, the midpoint is at height zero).

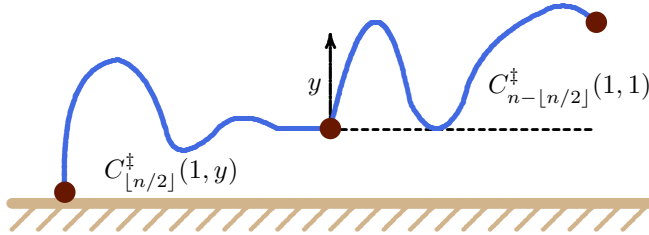


Figure 4. Concatenating two unfolded walks, the first pulled at its endpoint, gives a lower bound on $W_n(1, y)$ (that is, the partition function of a walk pulled in its midpoint).

Theorem 2. When $y \geq 1$ the limit

$$\lim_{n \rightarrow \infty} \frac{1}{n} \log W_n(1, y) \equiv \phi(1, y)$$

exists and $\phi(1, y) = \frac{1}{2}[\lambda(y) + \log \mu_d]$.

Proof: We can get an upper bound by regarding the two subwalks that meet at the midpoint as being independent and allowing the second sub-walk to penetrate the surface. This gives

$$\sum_v w_n(v, h) \leq \sum_v c_{[n/2]}^+(v, h) c_{n-[n/2]} \quad (12)$$

where c_m is the number of self-avoiding walks with m edges. Multiplying by y^h , summing over h , taking logarithms and dividing by n gives

$$\limsup_{n \rightarrow \infty} \frac{1}{n} \log W_n(1, y) \leq \frac{1}{2}[\lambda(y) + \log \mu_d]. \quad (13)$$

To get a lower bound we work with unfolded walks (see figure 4). If we concatenate an unfolded walk pulled at its end-point (with $\lfloor \frac{1}{2}n \rfloor$ edges) and an unfolded positive walk (with $n - \lfloor \frac{1}{2}n \rfloor$ edges) we have a subset of walks pulled at their mid-point so

$$W_n(1, y) \geq C_{[n/2]}^\dagger(1, y) C_{n-[n/2]}^\dagger(1, 1) \quad (14)$$

and therefore

$$\liminf_{n \rightarrow \infty} \frac{1}{n} \log W_n(1, y) \geq \frac{1}{2}[\lambda(y) + \log \mu_d] \quad (15)$$

which completes the proof. \square

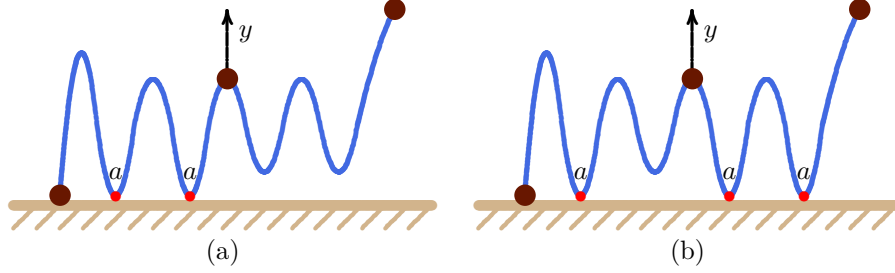


Figure 5. (a) An adsorbing walk pulled in its mid-point by a vertical force with last visit *before* the mid-point. (b) An adsorbing walk with visits *after* the mid-point (where it is pulled).

Theorem 3. When $a \leq 1$ and $y \geq 1$ the free energy of walks pulled at their mid-point is independent of a . That is $\lim_{n \rightarrow \infty} \frac{1}{n} \log W_n(a, y) \equiv \phi(a, y) = \phi(1, y)$ for all $a \leq 1$.

Proof: Fix $a \leq 1$. By monotonicity

$$W_n(0, y) \leq W_n(a, y) \leq W_n(1, y). \quad (16)$$

Consider walks pulled at their mid-point but unfolded in the x_1 -direction. Translate the walk unit distance in the positive x_d -direction, add an edge to reconnect to the origin and add an edge to the other end of the walk in the positive x_1 -direction. The resulting walk has no visits and the procedure can be reversed. In addition the height of the mid-point changes by 1. Hence

$$W_n^\dagger(1, y) = y^{-1} W_{n+2}^\dagger(0, y). \quad (17)$$

Then

$$y W_{n-2}^\dagger(1, y) = W_n^\dagger(0, y) \leq W_n(0, y) \leq W_n(a, y) \leq W_n(1, y) \quad (18)$$

and $W_n^\dagger(1, y) \leq W_n(1, y) \leq W_n^\dagger(1, y) e^{O(\sqrt{n})}$ and the theorem follows. \square

5. Desorbing a self-avoiding walk by applying a force at the middle vertex

In this section we shall be primarily concerned with the case $a \geq a_c$ and $y \geq 1$. We need a preliminary lemma.

Lemma 1. When a loop does not interact with the surface and is pulled in its highest plane

$$\lim_{n \rightarrow \infty} \frac{1}{n} \log L_n(1, y) = \lambda(\sqrt{y}).$$

Proof: Consider a loop with n edges. Let m be the last vertex of the loop in its top plane (*i.e.* with largest x_d -coordinate). Reflect the subwalk from the m th to the n th vertex in this plane to give a positive walk with its last vertex in its top plane. The height of this subwalk is twice the height of the original loop. This gives the inequality $\sum_v l_n(v, h) \leq \sum_v c_n^+(v, 2h)$ and consequently

$$L_n(1, y) \leq \sum_{v, h} c_n^+(v, 2h) y^h \leq \sum_{v, h} c_n^+(v, h) (\sqrt{y})^h = C_n^+(1, \sqrt{y}), \quad (19)$$

and therefore

$$\limsup_{n \rightarrow \infty} \frac{1}{n} \log L_n(1, y) \leq \lambda(\sqrt{y}). \quad (20)$$

To obtain a suitable lower bound we shall construct loops from pairs of unfolded bridges with the same height (which is also their span in the x_d -direction). With y fixed suppose that h^* is the value of h such that $b_n^\dagger(h^*)y^{h^*} \geq b_n^\dagger(h)y^h$ for all h . (Note that h^* depends on both n and y .) Then

$$\frac{B_n^\dagger(y)}{n} \leq b_n^\dagger(h^*)y^{h^*} \leq B_n^\dagger(y) \quad (21)$$

and therefore

$$\lim_{n \rightarrow \infty} \frac{1}{n} \log b_n^\dagger(h^*)y^{h^*} = \lambda(y). \quad (22)$$

Now concatenate an unfolded bridge with n edges and height h^* with another bridge, reflected in $x_1 = 0$ and translated, also with n edges and height h^* . The resulting object is a loop with $2n$ edges and span h^* . Hence

$$(b_n^\dagger(h^*))^2 y^{h^*} = (b_n^\dagger(h^*)\sqrt{y}^{h^*})^2 \leq L_{2n}(1, y). \quad (23)$$

Taking logarithms, dividing by $2n$ and letting $n \rightarrow \infty$ gives

$$\lambda(\sqrt{y}) \leq \liminf_{n \rightarrow \infty} \frac{1}{n} \log L_n(1, y). \quad (24)$$

Then (20) and (24) complete the proof. \square

This result will be used in the main theorem of this section.

Remark 1. *Essentially the same proof can be used to show that loops pulled at their mid-point, and that loops that have their mid-point in the top plane and are pulled at this mid-point, also have free energy equal to $\lambda(\sqrt{y})$.*

Theorem 4. *When $a \geq 1$ and $y \geq 1$*

$$\phi(a, y) = \lim_{n \rightarrow \infty} \frac{1}{n} \log W_n(a, y) = \max[\kappa(a), \frac{1}{2}(\lambda(y) + \log \mu_d)].$$

Proof: Fix $a \geq 1$ and $y \geq 1$. By monotonicity $W_n(a, y) \geq \max[W_n(a, 1), W_n(1, y)]$ so

$$\liminf_{n \rightarrow \infty} \frac{1}{n} \log W_n(a, y) \geq \max[\kappa(a), \frac{1}{2}(\lambda(y) + \log \mu_d)]. \quad (25)$$

For a walk pulled at its mid-point either the last visit to the surface is before (or at) the mid-point, or it is after the mid-point (see figure 5). If the last visit is before (or at) the mid-point (case (a) in figure 5), an upper bound on the partition function of these walks is obtained by cutting the walk in its mid-point into an adsorbing walk of length $\lfloor \frac{1}{2}n \rfloor$ pulled at its endpoint, and a walk of length $n - \lfloor \frac{1}{2}n \rfloor$. This gives the upper bound $C_{\lfloor n/2 \rfloor}^+(a, y) c_{n - \lfloor n/2 \rfloor}$ and

$$\begin{aligned} \lim_{n \rightarrow \infty} \frac{1}{n} \log(C_{\lfloor n/2 \rfloor}^+(a, y) c_{n - \lfloor n/2 \rfloor}) &= \frac{1}{2}(\max[\kappa(a), \lambda(y)] + \log \mu_d) \\ &= \max[\frac{1}{2}(\kappa(a) + \log \mu_d), \frac{1}{2}(\lambda(y) + \log \mu_d)]. \end{aligned} \quad (26)$$

The other case (case (b) in figure 5) is where the last visit is after the mid-point of the walk. The middle vertex where the walk is pulled is in a loop that only has its first and last vertices in $x_d = 0$. This partitions the walk into three subwalks:

- (i) a positive walk interacting with the surface that starts and end in the surface,
- (ii) a loop with only the first and last vertices in the surface and subject to a force, and
- (iii) a positive walk interacting with the surface but with no force.

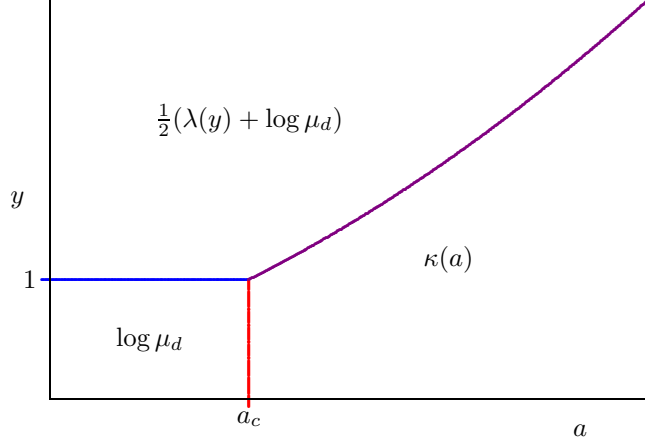


Figure 6. The phase diagram of adsorbing walks pulled at their midpoint. There are three phases: A free phase when $a < a_c$ and $y < 1$, a ballistic phase when $\phi(a, y) = \frac{1}{2}(\lambda(y) + \log \mu_d)$, and an adsorbed phase when $\phi(a, y) = \kappa(a)$. The phase boundary between the adsorbed and ballistic phases is given by the solution of $\kappa(a) = \frac{1}{2}(\lambda(y) + \log \mu_d)$.

Note that the loop containing the mid-point has vertical span at least as large as the height of the mid-point. If these three subwalks are treated independently we have the following upper bound on the partition function:

$$\begin{aligned}
 & ay \sum_{3 \leq m_2 \leq n} \sum_{0 \leq m_1 \leq m_2 - 3} C_{m_1}^+(a, 1) L_{m_2 - m_1 - 2}(1, y) C_{n - m_2}^+(a, 1) \\
 & \leq ay n^2 \max_{m_1, m_2} [e^{\kappa(a)m_1} e^{\lambda(\sqrt{y})(m_2 - m_1 - 2)} e^{\kappa(a)(n - m_2)} e^{o(n)}] \\
 & = ay n^2 \max_m [e^{\kappa(a)(n - m) + \lambda(\sqrt{y})(m - 2) + o(n)}].
 \end{aligned} \tag{27}$$

Thus, it follows that

$$\begin{aligned}
 & \limsup_{n \rightarrow \infty} \frac{1}{n} \log \left(ay \sum_{3 \leq m_2 \leq n} \sum_{0 \leq m_1 \leq m_2 - 3} C_{m_1}^+(a, 1) L_{m_2 - m_1 - 2}(1, y) C_{n - m_2}^+(a, 1) \right) \\
 & \leq \max[\kappa(a), \lambda(\sqrt{y})].
 \end{aligned} \tag{28}$$

Equations (26) and (28) then imply that

$$\limsup_{n \rightarrow \infty} \frac{1}{n} \log W_n(a, y) \leq \max[\kappa(a), \lambda(\sqrt{y}), \frac{1}{2}(\lambda(y) + \log \mu_d)] \tag{29}$$

since $\kappa(a) \geq \log \mu_d$. Since $\lambda(y)$ is a convex function of $\log y$

$$\lambda(\sqrt{y}) \leq \frac{1}{2}[\lambda(y) + \log \mu_d]. \tag{30}$$

Then equations (25), (29) and (30) complete the proof. \square

The phase boundary between the ballistic and adsorbed phase is the locus of the solution of the equation $\kappa(a) = \frac{1}{2}[\lambda(y) + \log \mu_d]$ for $a > a_c$ and $y > 1$. The argument given in [3] works *mutatis mutandis* to prove that this phase transition is first order.

These results, taken together, give considerable information about the form of the phase diagram in the (a, y) -plane and we give a sketch in figure 6.

6. Low temperature asymptotics

The results of Section 5 show that the phase boundary between the adsorbed and ballistic phases is given by the solution of the equation $\kappa(a) = \frac{1}{2}[\lambda(y) + \log \mu_d]$. We can say something useful about the low temperature limit because we know the behaviour of $\kappa(a)$ and $\lambda(y)$ when a and y are large [16, 23]. In fact $\kappa(a)$ is asymptotic to $\log a + \log \mu_{d-1}$ as $a \rightarrow \infty$ [23] and $\lambda(y)$ is asymptotic to $\log y$ as $y \rightarrow \infty$ [16]. Recalling that $a = \exp[-\epsilon/k_B T]$ and $y = \exp[f/k_B T]$ this gives

$$f_c(T) \rightarrow -2\epsilon + [2 \log \mu_{d-1} - \log \mu_d] k_B T \quad (31)$$

as $T \rightarrow 0$. At $T = 0$ the required force is twice as large as the force needed when the walk is pulled at its last vertex [16]. When $d = 3$ μ_3 is about 4.68 and μ_2 is about 2.638 [21] so $\lim_{T \rightarrow 0} df_c(T)/dT > 0$ and the force-temperature curve is re-entrant. When $d = 2$ $\mu_1 = 1$ so $\lim_{T \rightarrow 0} df_c(T)/dT < 0$ because the walk gains entropy in the ballistic phase. Compare this with the case of pulling at the last vertex [16] where $\lim_{T \rightarrow 0} df_c(T)/dT = 0$ when $d = 2$.

7. Pulling at other interior vertices

In this section we consider pulling at an interior vertex other than the middle vertex.

Suppose that we have a positive walk with n edges and we pull at the vertex labelled $m = \lfloor \alpha n \rfloor$, $0 < \alpha < 1$. Let $w_n^\alpha(v, h)$ be the number of positive walks with n edges, with $v + 1$ vertices in $x_d = 0$ and with x_d -coordinate of the m th vertex equal to h . Define the partition function $W_n^\alpha(a, y) = \sum_{v, h} w_n^\alpha(v, h) a^v y^h$. Clearly $\lim_{n \rightarrow \infty} \frac{1}{n} \log W_n^\alpha(a, 1) = \kappa(a)$.

The arguments developed in Sections 3 and 4 generalize easily to the case of a walk pulled at any interior vertex, $0 < \alpha < 1$. For $a \leq a_c$ and $y \leq 1$ the free energy is equal to $\log \mu_d$ and the system is in the *free phase*. When $y \leq 1$ the free energy is $\kappa(a)$, independent of y and when $a \leq 1$ and $y \geq 1$ the free energy is equal to $\alpha \lambda(y) + (1 - \alpha) \log \mu_d$, independent of a .

Fix $a \geq 1$ and $y \geq 1$. By repeating the argument in Section 5 for the case $\alpha = \frac{1}{2}$ it is easy to see that

$$\liminf_{n \rightarrow \infty} \frac{1}{n} \log W_n^\alpha(a, y) \geq \max[\kappa(a), \alpha \lambda(y) + (1 - \alpha) \log \mu_d]. \quad (32)$$

Similarly we can derive the corresponding upper bound

$$\limsup_{n \rightarrow \infty} \frac{1}{n} \log W_n^\alpha(a, y) \leq \max[\kappa(a), \lambda(\sqrt{y}), \alpha \lambda(y) + (1 - \alpha) \log \mu_d]. \quad (33)$$

If $\frac{1}{2} \leq \alpha \leq 1$ then $\lambda(\sqrt{y}) \leq \lambda(y^\alpha)$ and, since $\lambda(y)$ is a convex function of $\log y$, $\lambda(y^\alpha) \leq \alpha \lambda(y) + (1 - \alpha) \log \mu_d$. Consequently, using (32) and (33),

$$\lim_{n \rightarrow \infty} \frac{1}{n} \log W_n^\alpha(a, y) = \max[\kappa(a), \alpha \lambda(y) + (1 - \alpha) \log \mu_d] \quad (34)$$

for all $\alpha \geq \frac{1}{2}$ for $a \geq 1$ and $y \geq 1$.

This gives a complete description of the phase diagram when $\alpha > \frac{1}{2}$. When $\alpha < \frac{1}{2}$ our results are less complete but there are interesting differences. The key distinction in this situation is that a walk that is extended as far as possible by the applied force can still return to the adsorbing plane.

When $\alpha < \frac{1}{2}$ we shall proceed by constructing a strategy lower bound on the partition function. The idea is to consider the subset of walks where the walk leaves the surface at its first step and returns for the first time at vertex $2\lfloor \alpha n \rfloor$. Vertex $\lfloor \alpha n \rfloor$ is in the top plane of the loop from the origin to vertex $2\lfloor \alpha n \rfloor$. (Note that, by this definition, the vertex at which the force is applied is in the top plane of the loop.) We shall call these walks *LA-walks* to recall that the first part is a loop

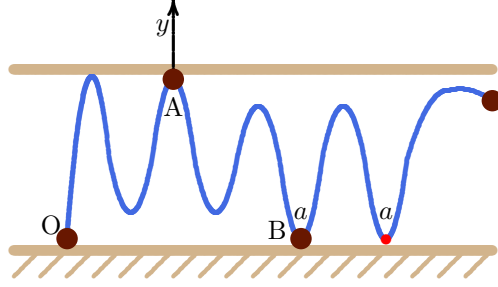


Figure 7. A schematic diagram of an LA -walk. The pulling force is applied at a vertex marked A in the top plane of the loop from O to B and is a distance $\lfloor \alpha n \rfloor$ along the walk from O . The walk returns for the first time to the adsorbing plane at B , and the length of the walk from O to B is $2\lfloor \alpha n \rfloor$. The remaining part of the walk, from B to its endpoint, is an adsorbing walk which is not directly affected by the pulling force at A . OAB is a loop of length $2\lfloor \alpha n \rfloor$ pulled in its midpoint which is also in the top plane of the loop.

pulled at its midpoint and the remainder is a walk that can adsorb with no force. For a sketch of an LA -walk see figure 7. Suppose that the partition function of these walks is $\mathcal{L}_n(a, y, \alpha)$.

Lemma 2. *The free energy of LA -walks is given by*

$$\chi_{LA}(a, y, \alpha) = \lim_{n \rightarrow \infty} \frac{1}{n} \log \mathcal{L}_n(a, y, \alpha) = 2\alpha\lambda(\sqrt{y}) + (1 - 2\alpha)\kappa(a).$$

Proof: The partition function of loops with $2\lfloor \alpha n \rfloor$ edges that have only their first and last vertices in the adsorbing surface, pulled in their top plane, is $yL_{2\lfloor \alpha n \rfloor - 2}(1, y)$. Concatenate these with positive walks with $n - 2\lfloor \alpha n \rfloor$ edges giving the upper bound

$$\limsup_{n \rightarrow \infty} \frac{1}{n} \log \mathcal{L}_n(a, y, \alpha) \leq 2\alpha\lambda(\sqrt{y}) + (1 - 2\alpha)\kappa(a). \quad (35)$$

We construct a lower bound by concatenating unfolded loops (pulled at their mid-point that is conditioned to be in their top plane) with unfolded positive walks, with an intermediate edge. The free energy of these loops is $\lambda(\sqrt{y})$ (see Remark 1). This gives

$$\liminf_{n \rightarrow \infty} \frac{1}{n} \log \mathcal{L}_n(a, y, \alpha) \geq 2\alpha\lambda(\sqrt{y}) + (1 - 2\alpha)\kappa(a) \quad (36)$$

and these two bounds complete the proof. \square

We shall now use this result to show that there are regions of the (a, y) -plane where the free energy is greater than $\max[\kappa(a), \alpha\lambda(y) + (1 - \alpha)\log \mu_d]$. We first observe that $\chi_{LA} > \kappa(a)$ if and only if $\lambda(\sqrt{y}) > \kappa(a)$. Now $\lambda(\sqrt{y}) \geq \frac{1}{2} \log y$ and $\kappa(a) \leq \log a + \log \mu_d$ so if

$$\log y > 2 \log a + 2 \log \mu_d \quad (37)$$

then $\lambda(\sqrt{y}) > \kappa(a)$.

Since $\lambda(y) \leq \log y + \log \mu_d$ and $\kappa(a) \geq \log a + \log \mu_{d-1}$ (see for instance [5]) we observe that the condition

$$\log a > \frac{\log \mu_d}{1 - 2\alpha} - \log \mu_{d-1} \quad (38)$$

implies that

$$\chi_{LA} > \alpha\lambda(y) + (1 - \alpha)\log \mu_d. \quad (39)$$

Hence if conditions (37) and (38) are both satisfied then we are assured that the free energy is larger than $\max[\kappa(a), \alpha\lambda(y) + (1-\alpha)\log\mu_d]$ and there is an additional phase in the phase diagram. For any $0 < \alpha < \frac{1}{2}$ both conditions can always be satisfied by making a and y sufficiently large. For instance, if $\alpha = \frac{1}{4}$ then sufficient conditions are $\log a > 2\log\mu_d - \log\mu_{d-1}$ and $\log y > 2\log a + 2\log\mu_d$.

8. Discussion

Earlier work has focused on pulling a terminally attached self-avoiding walk from a surface at which it is adsorbed by applying a force at the last vertex of the walk [3, 16, 19, 20, 22], or in the plane containing the vertices furthest from the surface [18]. From the experimental point of view there are interesting questions about how the behaviour depends on where the force is applied and, in this paper, we consider the case where the force is applied (normal to the surface) at the mid-point of the walk. We show that the phase diagram in the (a, y) -plane is qualitatively similar to that for the case where the force is applied at the last vertex but the phase boundary between the adsorbed and ballistic phases is shifted. That is, the critical force required for desorption depends on where the force is applied. When we switch to the force-temperature plane there are distinct differences in the low temperature behaviour depending on where the force is applied.

We have also considered the case where the force is applied at an interior vertex other than the middle vertex. Our results are less complete but we have shown that, in some circumstances, the critical force for desorption changes when we change the vertex at which the force is applied. When the force is applied between the middle vertex and the free vertex of degree 1 (not attached to the surface) the results depend on the particular vertex at which the force is applied, but the transition is from an adsorbed to a ballistic phase, as in the case when the force is applied at the middle vertex. When the force is applied between the middle vertex and the point of attachment we have shown that there is an intermediate phase for some values of a and y and we have bounds on these values. In this phase we have a lower bound on the free energy that should be especially effective at large a and y but it is unlikely that this bound will be strict throughout this phase. The walks in this phase are expected to consist of a loop that is extended by the force but the walk then returns to the surface and the remainder of the walk has a positive density of visits. LA-walks are a subset of these walks.

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